Lead-Free Soldering of

A host of lead-free solder replacements are coming to the fore, each presenting the user with certain tradeoffs. Many of the replacement solder systems are based on adding a small quantity of a third or fourth element to binary alloy systems to lower the solder's melting point, which increases wetting and reliability.

Packaging trends have progressively moved toward the smaller, faster, lighter and cheaper: from fine-pitch SMT to area-array packaging; and from ball grid array (BGA) to chip-scale packages and to flip chip.

Area-array packaging now provides great benefits at both the chip and component levels. CSPs are particularly attractive, in the sense that they deliver a nice balance between miniaturization and manufacturability.

The interconnect technology for BGAs and CSPs has also evolved over time. For CSPs, interconnecting solder materials are usually introduced at two stages. The first is a pre-deposit of solder onto the packaging, usually accomplished through solder bumping. The solder-bumped package is then mounted onto the next level of packaging through soldering.

The soldering process here may or may not need the introduction of additional solder materials. The additional materials may or may not be the same solder alloy as the solder bump on the packaging.

Although many methods have been developed, they can be roughly categorized into three groups:

1. Liquid-metal bonding (soldering)
2. Solid-metal bonding (wire bonding, TAB, etc.)
3. Metal-filled polymer bonding (anisotropic conductive adhesive, isotropic conductive adhesive, etc.)

Soldering is by far the preferred approach for interconnecting area-array packages. This is especially true for the second-level assembly stage of BGAs and CSPs.

Alloys Used for CSP Interconnects

The choice of solder alloys is determined by the requirements of both process and reliability.

Initially, besides meeting the solder wetting requirement, the solder chosen should be able to maintain its physical and mechanical integrity during subsequent processing. In this way, at the end of the packaging and assembly processes, the solder joints formed initially will not be altered or ruined.

When additional solder materials are needed, they are often introduced through either solder coating onto the next level of packaging or the use of solder-paste deposition as a bonding medium.

Alloys Used in FC Solder Bumping and Soldering

For flip-chip in component (FCIP), the solders utilized for FC solder bumping and joining must normally have high melting points, such as 97Pb3Sn or 95Pb5Sn. For direct chip attach (DCA) or flip-chip on board (FCOB) applications, the solders utilized for flip-chip bumping, as well as the solder coating on the next-level packaging, often are eutectic or near-eutectic lead/tin solders.

Alloys Used in BGA and CSP Solder Bumping and Soldering

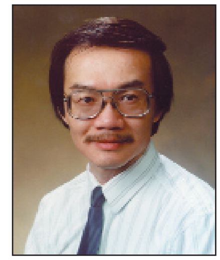
For heavy components, such as CCGA or CBGA devices, the solder used for either column or ball is typically 90Pb10Sn.

The column is mounted onto the CSP via either casting or 63Sn37Pb solder joining. For CBGAs, the 90Pb10Sn solder ball is typically mounted via 63Sn37Pb solder paste soldering.

The high melting point of 90Pb10Sn solder ensures the required standoff of CCGA or CBGA on PCBs during board-level soldering assembly using eutectic 63Sn37Pb or 62Sn36Pb2Ag solders.

For light components such as PBGA devices, the components are bumped with 63Sn37Pb or 62Sn36Pb2Ag and soldered onto the board, either with flux alone, or with solder pastes, using similar alloy systems.

Chip-Scale Packages



By Dr. Ning-Cheng Lee, Indium Corporation of America, Clinton, New York

With CSPs, the alloys used are similar to those employed with PBGAs. The use of solder paste, rather than flux alone, for board-level assembly is recommended.

Lead-Free Solders

Lead-free soldering for electronics is a global trend toward a lead-free environment, and the favored Pb-free solder alternatives vary from region to region.

In general, however, high-tin alloys are preferred. These include Sn/Ag, Sn/Cu, Sn/Ag/Cu, Sn/Ag/Bi and various versions of those alloys with small amounts of other elements, such as Sb.

Sn/Ag/Bi systems are currently employed in some Japanese products. However, Sn/Ag/Cu systems are more tolerant toward Pb contamination than bismuth-containing systems and are therefore more compatible with the existing infrastructure during this transition stage.

The application will dictate the specific Pb-free alloy chosen for different applications. Pb-free solder systems suitable for CSP soldering applications are primarily alloys of Sn with Ag, Bi, Cu, Sb, In or Zn, as shown in Table 1.

These alloys may serve as substitutes for eutectic Sn/Pb solders in CSP interconnects. However, substitutes for high-melting-temperature solders have not yet been developed.

Let's look at some of the more promising alloys, and their characteristic advantages and disadvantages, as applied to the CSP attachment process. Many of the systems are based on adding a small quantity of a third or fourth element to binary alloy systems to lower the alloy's melting point and increase wetting and reliability.

Researchers have reported that, with increasing amounts of additive elements, the melting point of the system first decreases. The bond strength then rapidly decreases, almost levels off, then decreases again. Finally, the wettability increases rapidly at first, reaching its maximum at a composition corresponding to the midpoint of the plateau of bond strength, before it decreases.

Note the following examples:

Sn99.3/Cu0.7

Sn99.3/Cu0.7 (227°C) is reported to have soldering qualities equal to eutectic Sn/Pb in telephone manufacturing. In air reflow, however, wettability is reduced, and the fillet exhibits a rough and textured appearance. This composition is probably the "poorest" in mechanical properties available from all Pb-free solders. This is best suited for use in wave soldering, because the materials cost and the inverting of waves is not costly.

Table 1. LEAD-FREE SOLDERS FOR CSP APPLICATIONS

Melting Temperature Range °(C)	Solder Alloy
227	99.3Sn0.7Cu
221	96.5Sn3.5Ag
221–226	98Sn2Ag
205–213	93.5Sn3.5Ag3Bi
207–212	90.5Sn7.5Bi2Ag
200–216	91.8Sn3.4Ag4.8Bi
226–228	97Sn2Cu0.8Sb0.2Ag
213–218	96.2Sn2.5Ag0.8Cu0.5Sb
232–240	95Sn5Sb
189–199	89Sn8Zn3Bi
138	58Bi42Sn
217–219	95.5Sn4Ag0.5Cu
216–218	93.6Sn4.7Ag1.7Cu
217–219	95.5Sn3.8Ag0.7Cu
217–218	96.3Sn3.2Ag0.5Cu
217–219	95Sn4Ag1Cu

Sn96.5/Ag3.5

Sn96.5/Ag3.5 (221°C) is considered one of the most promising by NCMS, Ford, Motorola and TI Japan. A German study[1] suggests that it is one of the most suitable alloys. There is a long history of use for this alloy. Indium Corp., however, reported that it offers the poorest wetting for reflow soldering among high-Sn alloys.

Sn/Ag/Cu

This is a ternary eutectic at 217°C, although the exact composition is to be clarified. Cu is added to Sn/Ag to slow the Cu dissolution and lower the melting temperature. This improves wettability, creep and thermal fatigue characteristics. Nokia and Multicore found that yields and reliability are comparable to or better than eutectic Sn/Pb alloy[2]. The Brite-Euram project reported better reliability and solderability than Sn/Ag and Sn/Cu, and recommended this alloy for general-purpose use[3].

Sn/Ag/Cu/X

Sn96.2/Ag2.5/Cu0.8/Sb0.5 (213-218°C, AIM, Castin Alloy) is reported by the International Tin Research Institute, Ford, Lucent and Sandia Labs to have greater fatigue performance than a eutectic Sn/Pb alloy[4]. The Brite-Euram Project reported that a 0.5% Sb addition may strengthen the alloy further. Sn97/Cu2/Sb0.8/Ag0.2 (226–228°C, Kester, SAF-ALLOY) may be considered for wave- and hand-soldering applications. Sn/Ag/Cu/In (Tamura) may also be promising.

Sn/Ag/Bi/X

The addition of ≤ 5% Bi lowers the melting point and improves the wettability of Sn/Ag systems.

With this alloy, solderability is the best among a range of Pb-free materials, confirmed by Indium Corp., and Matsushita. NCMS observed fillet lifting at through-hole joints as a concern for wave soldering, although other alloys, such as Sn96.5/Ag3.5, also suffer fillet lifting to a lesser extent.

Fillet lift is caused by the mismatch in TCE between solder and PWB materials and is aggravated by solders with a pasty range. It can be altered by the addition of other elements.

The addition of Cu and/or Ge results in strength improvement and possibly a wettability improvement. Adding Pb to Sn/Bi alloys can cause a 96°C ternary eutectic Bi52/Pb32/Sn16 to form. Calculations predict that at a fixed 6% Pb, even alloys with ≤ 4.8% Bi can have this eutectic liquid form, hence one should avoid Sn/Pb surface finishes.

The addition of a large amount (~5–20%) of Bi lowers the melting point of eutectic Sn/Pb solders but loses the good properties of eutectic Sn/Ag systems. Moreover, low temperature eutectic Bi58/Sn42, which has a low partial melting point (138°C), occurs. There are also reliability concerns, such as interfacial problems, with plating containing Pb on the electrodes of electronic components.

Sn/Sb

Sn95/Sb5 (232–240°C) offers poor wetting, although better than Sn96.5/Ag3.5, and its liquidus temperature is too high.

Sn/Zn/X

Sn91/Zn9 (eutectic 199°C) is fairly reactive, since Zn causes oxidation and corrosion, and reacts with flux to form a hardened paste. In Sn89/Zn8/Bi3, Bi replaces Zn to reduce the Zn corrosion in humid conditions. Sn/Zn/Bi alloys can have a melting point close to eutectic Sn/Pb. This alloy was developed primarily by home electronics manufacturers targeting low-cost products.

Sn/Bi

Bi58/Sn42 (138°C) is recommended by NCMS as a promising replacement, and eutectic Bi58/Sn42 is unusually resistant to coarsening. It is reported by HP[5] to have properties equivalent to or better than eutectic Sn/Pb. It shows promise for low-temperature applications or some consumer products.

The addition of 1% Cu dramatically slows the coarsening of eutectic Sn/Bi. The concerns, however, include eutectic Bi52/Pb32/Sn16 (96°C) formed on Pb surface finishes, furthermore, Bi is a by-product of Pb mining.

The Cost of Pb-Free Alloys

The cost of solder bar is dictated by the cost of raw materials (Table 2). However, for fabricated products such as solder pastes, the processing cost of manufacturing this material can become a dominant factor, and the difference between Sn/Pb and Pb-free materials becomes very small.

Thermal Damage

There is more to ponder about the substitution of Pb-free alloys in CSP soldering besides simply phasing out lead.

Since most of the promising alloy alternatives require a higher processing temperature, whether the components or substrates used can sustain the process becomes a big question.

Table 2.
RELATIVE COST OF LEAD-FREE SOLDER MATERIALS

Solder Alloy	Bar Relative Cost ($/Kg)	Paste Relative Cost ($/Kg)
Sn63/Pb37	1	1
Sn96.5/Ag3.5	2.29	1.07
Sn95/Ag3/Bi2	2.17	1.06
Sn96.1/Ag2.6/Cu0.8/Sb0.5	2.06	1.05
Sn91.8/Ag3.4/Bi4.8	2.26	1.06
Sn95/Ag3.5/Cu0.5/Zn1	2.27	1.06
Sn93.6/Ag4.7/Cu1.7	2.56	1.08
Sn96.1/Ag3.2/Cu0.7	2.21	1.06
Sn95.2/Ag3.5/Cu1.3	2.28	1.06

* Relative cost of selected metals:
Pb - 1, Zn - 1.7, Cu - 3, Sb - 3.9, Bi - 8.6, Sn - 11, Ag - 260, Au - 15000

For instance, electrolytic capacitors are highly susceptible to high-temperature damage.

Wound components, such as relays, are also susceptible to high-temperature damage. It is also considered likely that plastic-encapsulated ICs may show an increased tendency to "popcorn," as the alloy nears its expiration date.

Additionally, parametric damage to memory ICs processed at around 250°C is possible. As mentioned earlier, PWB and BGA polymeric substrates and solder masks may also suffer from higher processing temperatures. This is particularly true for flexible circuitry. The plastic insulation of connectors may also become distorted.

The corrosion and electromigration tendencies of Pb-free alloys need to be measured. Pastes and fluxes need to be evaluated. Since solder without Pb is different in appearance and is more difficult to monitor via X-ray, new standards for visual and X-ray inspection are needed, especially with packages such as BGAs, where X-ray inspection of visually inaccessible areas may be commonplace.

Conclusion

There are a number of promising Pb-free alloys that may be considered viable for soldering CSPs.

The appropriate alloy for the job will depend in many ways on the individual application, the width of its process window, the limitations (such as thermal), placed on the process by the CSP packages used, the PWB material, etc.

Process development on the part of the individual manufacturer is needed to determine which alloy will ultimately be the most appropriate replacement.

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Dr. Lee is vice president of technology for Indium Corp. Prior to joining Indium in 1986, he was at Morton Chemical and SCM.

He has spent more than 14 years in the development of fluxes and solder pastes for SMT industries. Dr. Lee received a bachelors degree in chemistry from the National Taiwan University and received his Ph.D. in polymer science from the University of Akron (Ohio). Readers may contact him at nclee@indium.com or by phone at 315.853-4900.

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